

Ferroelectric phase transition in orthorhombic CdTiO₃: First-principles studies

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The crystal structures and phonon spectra of orthorhombic cadmium titanate with the $Pbnm$ structure and of its two possible ferroelectrically distorted phases with $Pbn2_1$ and $Pb2_1m$ space groups were calculated from first principles within the density functional theory. The obtained structural parameters and frequencies of Raman- and infrared-active modes are in good agreement with available experimental data for the $Pbnm$ phase. Expansion of the total energy in a Taylor series of two order parameters showed that the ground state of the system corresponds to the $Pbn2_1$ structure into which the $Pbnm$ phase transforms through a second-order phase transition without intermediate phases. A substantial discrepancy between the calculated and experimentally observed lattice distortions and spontaneous polarization in the polar phase was explained by quantum fluctuations as well as by existence of twinning and competing long-period structures.

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I. INTRODUCTION

The calculations of phonon spectra of ten titanates $ATiO_3$ ($A = \text{Ca, Sr, Ba, Ra, Cd, Zn, Mg, Ge, Sn, Pb}$) with the perovskite structure in Ref. 1 have revealed that orthorhombic phases of CdTiO_3 , ZnTiO_3 , and MgTiO_3 with the $Pbnm$ structure exhibit the ferroelectric instability which appears in their phonon spectra as one or two unstable modes with symmetries B_{1u} and B_{2u} at the Γ point. In this work, the characteristics of these modes are considered and the results of first-principles calculations of the crystal structure, phonon spectra, and spontaneous polarization of the parent orthorhombic CdTiO_3 phase with $Pbnm$ structure and its two ferroelectrically distorted orthorhombic modifications (with $Pbn2_1$ and $Pb2_1m$ space groups) are compared with available experimental data.

The ferroelectric phase transition in cadmium titanate was discovered by Smolenskii² in 1950. Since then, this phase transition was studied by dielectric^{3–6} and X-ray^{3,4,7} methods; using Raman scattering;^{3,8} IR and sub-millimeter reflectance spectroscopy;⁹ pyroelectric current measurements.⁴ The specific features of the phase transition in CdTiO_3 are a smallness of the lattice distortions and a considerable scatter in the data on the phase transition temperature (50–82 K) and spontaneous polarization (0.002–0.009 C/m²). Even the data on the structure of the low-symmetry phase are contradictory. In particular, the study of the dielectric properties⁶ suggests that the $2_1/m$ axis becomes polar, whereas structural studies using synchrotron radiation suggest that it is the $2_1/n$ axis that becomes polar.⁷ In Refs. 5, 8, and 9, the analysis of the temperature dependence of the dielectric constant and the Raman lines intensity allowed the authors to suggest that upon cooling one more phase transition accompanied by a change in the polarization direction occurs in CdTiO_3 at about 50 K.

The paper by Fabricius and López García¹⁰ is the only work in which CdTiO_3 was studied from first principles.

In this work, the authors calculated the electric field gradient at cadmium atoms for different sets of atomic coordinates proposed in the literature for $Pbnm$ and $Pbn2_1$ structures and revealed that the latter structure transforms into a more stable nonpolar $Pbnm$ phase during relaxation.

In view of the discrepancies between the experimental data available in the literature for cadmium titanate, it is expedient to perform first-principles calculations in order to elucidate the causes responsible for these contradictions and to resolve them.

II. CALCULATION TECHNIQUE

The calculations were performed within the density functional theory with the pseudopotentials and the plane-wave expansion of wave functions as implemented in the ABINIT code.¹¹ The exchange-correlation interaction was described in the local-density approximation (LDA).¹² As pseudopotentials, we used the optimized separable nonlocal pseudopotentials,¹³ generated with the OPIUM code, to which the local potential was added in order to improve their transferability.¹⁴ The parameters used for constructing the pseudopotentials, the results of their testing, and other details of calculations are described in Ref. 1.

III. RESULTS OF THE CALCULATIONS

A. Phonon spectrum of the $Pbnm$ phase

The calculated frequencies of the softest phonons at the Γ point, which are responsible for the ferroelectric instability in orthorhombic CaTiO_3 , CdTiO_3 , ZnTiO_3 , and MgTiO_3 compounds with the $Pbnm$ structure and in tetragonal SrTiO_3 with the $I4/mcm$ structure, are given in Table I. In CaTiO_3 and SrTiO_3 , all phonons are

TABLE I. Calculated frequencies (in cm^{-1}) of the softest ferroelectric modes in four titanates with the orthorhombic $Pbnm$ structure and tetragonal strontium titanate.

Mode	SrTiO ₃	CaTiO ₃	CdTiO ₃	ZnTiO ₃	MgTiO ₃
A_{2u}	55	—	—	—	—
E_u	39	—	—	—	—
B_{3u}	—	82	54	73	115
B_{2u}	—	97	81 <i>i</i>	54 <i>i</i>	81
B_{1u}	—	82	104 <i>i</i>	103 <i>i</i>	133 <i>i</i>
Γ_{15}	68 <i>i</i>	165 <i>i</i>	187 <i>i</i>	240 <i>i</i>	260 <i>i</i>

Note: The frequencies of unstable TO phonons at the Γ point of the Brillouin zone in the cubic parent phases are shown in the lowest row.¹

TABLE II. Lattice parameters a , b , and c (in Å) and atomic coordinates for CdTiO₃ with the $Pbnm$ structure.

Parameter	This work	Experiment	
		Ref. 15	Ref. 7*
a	5.2427	5.3053	5.284
b	5.3815	5.4215	5.403
c	7.5744	7.6176	7.590
Cd _{x}	-0.01017	-0.00847	-0.00891
Cd _{y}	+0.04637	+0.03873	+0.03997
Cd _{z}	+0.25000	+0.25000	+0.25000
Ti _{x}	+0.00000	+0.00000	+0.00000
Ti _{y}	+0.50000	+0.50000	+0.50000
Ti _{z}	+0.00000	+0.00000	+0.00000
O1 _{x}	+0.10130	+0.0902	+0.0918
O1 _{y}	+0.46252	+0.4722	+0.4714
O1 _{z}	+0.25000	+0.25000	+0.2500
O2 _{x}	+0.69348	+0.7008	+0.70083
O2 _{y}	+0.30304	+0.2969	+0.29660
O2 _{z}	+0.05341	+0.0472	+0.04783

* At $T = 150$ K.

stable (this corresponds to experiment), whereas in the other three titanates one or two unstable modes (whose frequencies are imaginary) arise. The strongest instability in these compounds is associated with the B_{1u} phonon, which can induce the $Pbnm \rightarrow Pbn2_1$ phase transition. In CdTiO₃ and ZnTiO₃, the phonon with the B_{2u} symmetry is also unstable. This phonon can induce the $Pbnm \rightarrow Pb2_1m$ phase transition. It should be noted that, among the three compounds under consideration, the $Pbnm$ structure can be obtained only for CdTiO₃ (ZnTiO₃ and MgTiO₃ usually crystallize in the ilmenite structure). This is why hereafter only the properties of cadmium titanate will be considered.

The calculated lattice parameters and equilibrium atomic coordinates for orthorhombic CdTiO₃ with the $Pbnm$ structure are compared with available experimental data in Table II. It is seen that the results of the

calculations are in good agreement with the experimental data. It should be noted that a better agreement is observed for the experimental data obtained at lower temperatures. A small systematic underestimation of the calculated lattice parameters is typical of the LDA approximation used in this work.

The vibrational spectrum of a crystal with the $Pbnm$ space group consists of 60 modes, including 24 Raman-active modes (with symmetries A_g , B_{1g} , B_{2g} , and B_{3g}), 25 IR-active optical modes (with symmetries B_{1u} , B_{2u} , and B_{3u}), 8 so-called silent A_u optical modes, and three acoustic modes inactive in the optical spectra.

The calculated frequencies of modes active in IR reflectance and Raman scattering are compared with available experimental data^{3,8,9} in Table III. For the Raman-active modes, the results of the calculations agree well with the experimental data obtained on ceramic samples³ and single crystals;⁸ the typical relative deviation of frequencies is about 3%. A comparison of the mode frequencies determined from polarized Raman scattering spectra⁸ with the results of our calculations shows that the peaks observed at 303 and 392 cm^{-1} in the yy polarization (in the crystal setting accepted in Ref. 8) is most likely erroneously assigned to the B_{1g} modes (in our crystal setting). The positions of these peaks are close to the positions of the peaks of the A_g modes, which can also be observed in the above polarization. The experimental peak at 307 cm^{-1} in the yz polarization, assigned to the B_{2g} or B_{3g} modes, is most likely a “leak” of the A_g mode.

A comparison of the calculated mode frequencies with the results obtained from an analysis of IR reflectance spectra⁹ appeared to be a more complex problem. A direct comparison of the experimental frequencies with the frequencies calculated for the symmetries of modes indicated in Ref. 9 revealed their significant disagreement. In order to reliably identify the experimentally observed modes, the oscillator strength f_i was additionally calculated for each mode (the oscillator strength characterizes the contribution of the mode into the complex dielectric constant) and it was supposed that in Ref. 9 the symmetries of the observed modes were identified incorrectly. This can be a result of the high twin density characteristic of CdTiO₃ crystals,^{8,15,16} which can undoubtedly manifest itself in measurements on samples with a large area.

The calculated frequencies and oscillator strengths for the CdTiO₃ crystal with the $Pbnm$ structure are compared with the results of the IR reflectance spectra studies in Fig. 1. Under the assumption that the modes identified as B_{3u} in Ref. 9 for the $Pnma$ crystal setting correspond to the B_{1u} modes in our $Pbnm$ setting and that the B_{1u} modes in Ref. 9 correspond to the B_{2u} and B_{3u} modes in our setting, the agreement between the calculated and experimental data becomes more reasonable (Fig. 1, Table III). A considerable shift in frequencies of three softest B_{1u} modes and two softest B_{2u} modes as compared to the calculated frequencies is explained by anharmonicity. The modes with calculated frequencies

TABLE III. Frequencies ν_i of the optical modes active in Raman and IR reflectance spectra and oscillator strengths f_i for IR-active modes in CdTiO₃ with the $Pbnm$ structure.

Mode	ν_i (cm ⁻¹)			Mode	$f_i \cdot 10^3$, arb. units	ν_i (cm ⁻¹)	
	This work	Exp. (Ref. 3)	Exp. (Ref. 8)			This work	Exp. (Ref. 9)
A_g	96	95	99	B_{3u}	3.87	54	61?
	128	123	125		1.27	104	111
	195	190	194		0.60	167	165
	295	295	299		0.38	275	284
	414	390	390		0.30	302	306
	449	461	465		0.71	379	383
	512	—	496		0.13	423	—
B_{3g}	140	135,141	144	B_{2u}	0.17	445	458
	211	—	—		0.96	513	525
	353	342	346		5.98	81i	61**
	486	—	479*		0.62	90	111**
	683	—	—		0.86	177	177
B_{2g}	117	—	114	B_{1u}	0.01	202	—
	280	—	307?		0.37	321	321
	445	—	459*		0.14	345	349
	488	—	509*		0.12	437	—
	764	—	—		1.04	476	483
B_{1g}	111	110	115		0.02	530	525
	142	141	141		3.42	104i	44**
	205	—	—		0.89	60	96**
	356	—	—		0.78	128	143**
	448	—	—		1.24	224	225
	492	—	504		0.62	396	387
	738	—	—		0.02	428	—
					1.19	481	511

* Components of a broad weakly structured line.

** A strong deviation from the calculations is a result of anharmonicity.

of 54 and 104 cm⁻¹ are most likely indistinguishable in the experiment from the other modes, and four modes with the smallest oscillator strengths are not observed in the spectra at all.

B. Lattice distortions accompanying the ferroelectric phase transitions

As shown above, the used technique of first-principles calculations describes well the properties of orthorhombic CdTiO₃ with the $Pbnm$ structure. Now, we consider the properties of ferroelectrically distorted phases of cadmium titanate. The equilibrium atomic positions in the distorted phases were determined by relaxing the Hellmann–Feynman forces in structures obtained from the parent nonpolar $Pbnm$ phase by adding a perturbation with the B_{1u} symmetry (for the $Pbn2_1$ phase) or B_{2u} symmetry (for the $Pb2_1m$ phase). The structure of the nonpolar $Pbnm$ phase and the character of atomic displacements accompanying the transitions from it to the

low-symmetry phases are shown in Fig. 2. The transition to the $Pb2_1m$ phase is accompanied by out-of-phase displacements of the titanium and oxygen atoms along the y axis, whereas the cadmium atoms remain almost unmoved. Upon the transition to the $Pbn2_1$ phase, both metal atoms are slightly displaced along the z axis (by approximately equal distances), and the displacements of the titanium and oxygen atoms contain a considerable y -component in addition to the z -component.

The transition to the polar phases results in the appearance of two nonequivalent sets of oxygen atoms O2 (labeled by the a and b letters in Table IV), and the disappearance of the n plane upon transition to the $Pb2_1m$ phase results in the appearance of two nonequivalent cadmium atoms (Cd1, Cd2). The energy gain (per formula unit) associated with the distortions is equal to 6.21 meV for the $Pbn2_1$ phase and 1.38 meV for the $Pb2_1m$ phase.

A comparison of the calculated atomic displacements and the lattice strains with the results of low-temperature X-ray measurements^{4,7} (Table IV) demonstrates that the atomic displacements and the lattice strains in the exper-

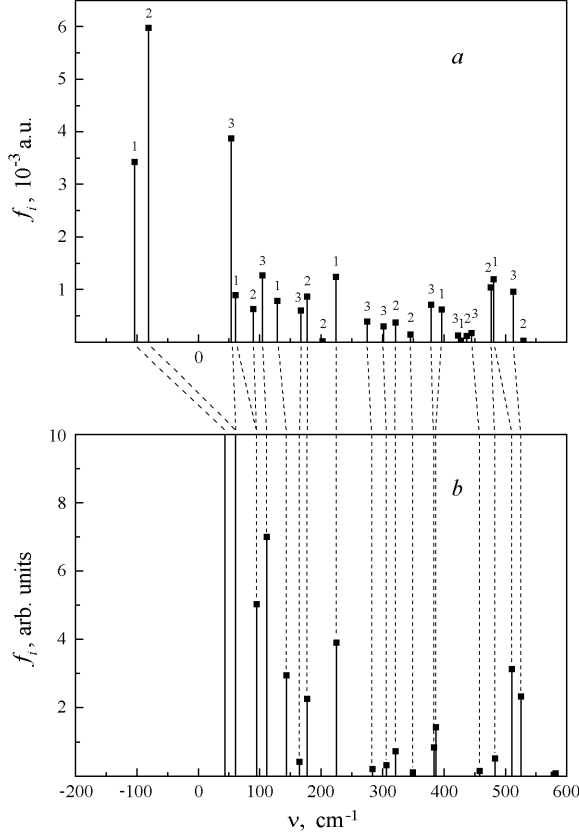


FIG. 1. Comparison of (a) the calculated frequencies and oscillator strengths of the IR-active modes for cadmium titanate with the $Pbnm$ structure with (b) the corresponding parameters obtained from an analysis of the IR reflectance spectra. Labels near the points indicate the mode symmetry (B_{1u} , B_{2u} , B_{3u}).

iment are much smaller. For example, from the comparison of the calculated lattice parameters in Tables II and IV it follows that a considerable increase (by 0.045 Å) in the lattice parameter along the polar c axis should be observed in the $Pbn2_1$ phase, and the a lattice parameter rather than the b lattice parameter should be increased in the $Pb2_1m$ phase. In the experiment, the largest spontaneous strain below the phase transition temperature was observed for the b lattice parameter (elongation of the order of 0.002 Å),⁴ which disagrees with the predictions for both ferroelectric phases. The possible causes of these discrepancies will be discussed below.

C. Parameters of an effective Hamiltonian

Torgashev et al.⁸ and Gorshunov et al.⁹ have supposed that below the ferroelectric phase transition temperature, one more phase transition accompanied by a change in the polarization direction occurs in cadmium titanate. In order to check this hypothesis, we calculated the de-

TABLE IV. Lattice parameters a , b , and c (in Å) and atomic coordinates for ferroelectrically distorted $Pbn2_1$ and $Pb2_1m$ phases of cadmium titanate.

Parameter	$Pbn2_1$		$Pb2_1m$	
	This work	Exp. (Ref. 4)	This work	Exp. (Ref. 7)
a	5.2392	5.2946	5.2498	5.281
b	5.3777	5.4151	5.3870	5.403
c	7.6192	7.6029	7.5699	7.583
$Cd1_x$	-0.01101	-0.0083	-0.01400	-0.01106
$Cd1_y$	+0.04425	+0.0407	+0.04583	+0.04076
$Cd1_z$	+0.25324	+0.25	+0.25000	+0.25000
$Cd2_x$	+0.01101	+0.0083	+0.00509	+0.00697
$Cd2_y$	-0.04425	-0.0407	-0.04696	-0.04076
$Cd2_z$	+0.75324	0.75	-0.25000	-0.25000
Ti_x	+0.00080	+0.004	+0.00459	+0.00190
Ti_y	+0.49548	+0.493	+0.50699	+0.5045
Ti_z	+0.00334	+0.004	+0.00080	+0.00214
$O1a_x$	+0.10277	+0.091	+0.10313	+0.0925
$O1a_y$	+0.46191	+0.473	+0.45559	+0.4759
$O1a_z$	+0.24044	+0.241	+0.25000	+0.25000
$O1b_x$	-0.10277	-0.091	-0.09897	-0.0911
$O1b_y$	-0.46191	-0.473	+0.53144	+0.5338
$O1b_z$	+0.74044	+0.741	-0.25000	-0.25000
$O2a_x$	+0.68779	+0.723	+0.69372	+0.6999
$O2a_y$	+0.31805	+0.308	+0.29494	+0.2951
$O2a_z$	+0.04267	+0.047	+0.05436	+0.0501
$O2b_x$	+0.29839	+0.323	+0.30806	+0.2989
$O2b_y$	+0.71471	+0.710	+0.68835	+0.7017
$O2b_z$	-0.06583	-0.045	-0.05264	-0.0457

* Correct signs of atomic displacements are recovered.

pendence of the total energy of the crystal on the lattice distortion with the B_{1u} and B_{2u} symmetries.

As is known, the normal modes form a complete basis set using which any combination of atomic displacements can be expanded. We expanded the lattice distortions in the $Pbn2_1$ and $Pb2_1m$ phases determined in Sec. IIIB using the basis of eigenvectors of the dynamic matrix of $CdTiO_3$ with the $Pbnm$ structure. For the $Pbn2_1$ phase, this expansion contains the contributions of seven modes with the B_{1u} symmetry (the acoustic B_{1u} mode that describes a uniform shift of the unit cell was excluded) and seven fully symmetric A_g modes (Fig. 3). For the $Pb2_1m$ phase, the expansion contains the contributions of nine B_{2u} modes (also without the acoustic mode) and seven A_g modes. In both cases, the contributions of the lowest-frequency modes with B_{1u} and B_{2u} symmetries to the total energy of distortions amount to 92.8 and 95.4%, respectively. Therefore, when constructing an effective Hamiltonian, we can restrict ourselves to the expansion in powers of the amplitudes of these two modes.

The total energy of the crystal was expanded in a Taylor series in powers of the distortion amplitudes ξ and

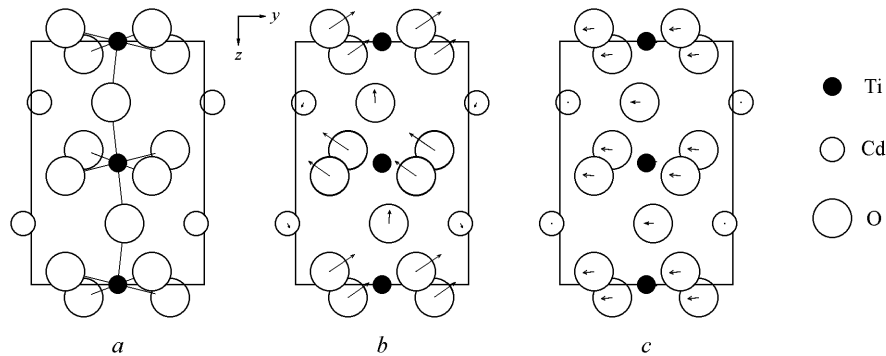


FIG. 2. (a) Projection of the structure of the orthorhombic CdTiO_3 phase with the $Pbnm$ structure onto the bc plane and (b, c) the character of atomic displacements accompanying the ferroelectric transitions to the (b) $Pbn2_1$ and (c) $Pb2_1m$ phases.

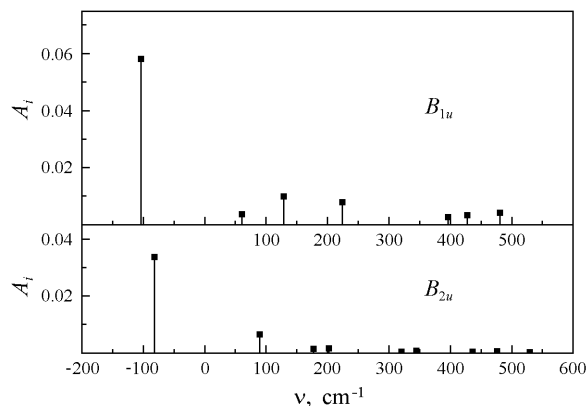


FIG. 3. Relative contributions of different modes with B_{1u} and B_{2u} symmetries to the ferroelectric distortions accompanying the transitions to the $Pb2_1m$ and $Pbn2_1$ phases of cadmium titanate.

η of the lowest-frequency normal modes with B_{1u} and B_{2u} symmetries. In this expansion, the lattice parameters were assumed to be fixed and equal to the lattice parameters of the $Pbnm$ phase. The resulting expansion had the form

$$E_{\text{tot}}(\xi, \eta) = E_{\text{tot}}(0, 0) + b_1 \xi^2 + c_1 \xi^4 + b_2 \eta^2 + c_2 \eta^4 + d \xi^2 \eta^2 \quad (1)$$

with the coefficients $b_1 = -0.4075$ Ha (Hartree), $b_2 = -0.2614$ Ha, $c_1 = 183.49$ Ha, $c_2 = 249.58$ Ha, and $d = 457.4$ Ha. It turned out that the total energy is adequately described by the fourth-order polynomials of two order parameters and that there is no need to include the sixth-order invariants into the expansion. This means that the phase transition in CdTiO_3 is far from the tricritical point (the closeness to which was supposed in Ref. 5). Furthermore, since we have $d > 2\sqrt{c_1 c_2}$, the minima of the total energy correspond to the order parameters $\pm(\xi, 0)$ and $\pm(0, \eta)$ and are separated from each other by the energy barriers. This means that the for-

mation of the monoclinic phase with Pb space group and tilted polarization vector is energetically unfavorable. The calculation using the formula (1) shows that the energy minima are observed at the mode amplitudes of $(\xi = 0.03332, \eta = 0)$ and $(\xi = 0, \eta = 0.02288)$ and that the energy gains associated with these lattice distortions are 6.16 and 1.86 meV, respectively. They are close to the corresponding energy gains of the true distortions (see Sec. III B).

Since only two modes with the lowest frequencies were included in expansion (1), it was necessary to check that the energetically most favorable $Pbn2_1$ phase remains stable with respect to small distortions with the B_{2u} symmetry when taking into account all modes involved in the distortion. For this purpose, we calculated the phonon spectrum of CdTiO_3 in the $Pbn2_1$ phase. In this spectrum, the ferroelectric mode polarized along the y axis had the lowest frequency of 83 cm^{-1} . The positive values of all mode frequencies confirm that the polar $Pbn2_1$ phase is the ground-state structure of CdTiO_3 .

Although the above analysis of the polar $Pbn2_1$ phase stability is for $T = 0$, it is unlikely that a change of the c_1 , c_2 , and d coefficients in the thermodynamic potential with increasing temperature can result in the violation of the $d > 2\sqrt{c_1 c_2}$ condition and the transition into the monoclinic phase. Therefore, the possibility of successive ferroelectric phase transitions in CdTiO_3 with varying temperature can be most likely ruled out. Possibly, the specific features observed in the dielectric constant of CdTiO_3 near 50 K ^{3,5,6} are associated with the existence of side minima of the total energy that are separated from the main minima by low potential barriers.

D. Spontaneous polarization

The spontaneous polarization P_s in the orthorhombic $Pbn2_1$ and $Pb2_1m$ phases of cadmium titanate was calculated by the Berry's phase method.¹⁷ The calculated values of P_s corresponding to the lattice distortions determined in Sec. III B for the $Pbn2_1$ and $Pb2_1m$ phases

are equal to 0.29 and 0.21 C/m², respectively. The spontaneous polarization P_s corresponding to the minima in expansion (1) is equal to 0.21 C/m² for the $Pbn2_1$ phase and 0.16 C/m² for the $Pb2_1m$ phase. It is worth noting that both calculated values of P_s considerably exceed the experimentally obtained polarizations of 0.002–0.009 C/m² (Refs. 4 and 5).

IV. DISCUSSION

As shown in Ref. 1, the ferroelectric instability is characteristic of cubic phases of all ten titanates with the perovskite structure studied in the cited work. In five of these compounds, which undergo structural phase transitions to the $Pbnm$ or $I4/mcm$ phases, the ferroelectric instability is weakened and can be observed only in three compounds with the $Pbnm$ structure: CdTiO₃, ZnTiO₃, and MgTiO₃ (Table I). A comparison of the frequencies of the softest ferroelectric modes at the Γ point in the cubic parent phases and in the $Pbnm$ or $I4/mcm$ phases shows that upon the structural phase transition, the ferroelectric instability is retained in crystals in which it is strongest in the cubic phase. Therefore, it is not surprising that the temperature of the ferroelectric phase transition in CdTiO₃ is considerably lower than in BaTiO₃ or PbTiO₃.

Studies of SrTiO₃ have long established that despite the existence of the ferroelectric instability in this compound, the corresponding phase transition does not occur with decreasing temperature. It is believed that such a behavior is due to quantum fluctuations, i.e., zero-point vibrations of atoms.¹⁸ One more factor responsible for this behavior can be the structural phase transition that occurs in this compound, which, as shown above, weakens the ferroelectric instability.

It is possible that the strong influence of quantum fluctuations on the physical properties of crystals should also be observed in CdTiO₃. As shown in Ref. 19, quantum effects most strongly affect the modes with a small “reduced mass,” in particular, the ferroelectric mode to which light oxygen atoms make a significant contribution. This explains why the substitution of the ¹⁶O isotope by the heavier ¹⁸O isotope in strontium titanate results in a real ferroelectric phase transition.²⁰

In order to take into account quantum fluctuations, expression (1) for the “potential” energy should be complemented by the kinetic energy of nuclei. When performing first-principles calculations, this energy is ignored in order to calculate correctly the forces acting on atoms (the Born–Oppenheimer approximation).

Although the approach used below requires a more rigorous justification, it is possible to try (following Ref. 19) to take into account quantum fluctuations at the level of the mode motion by adding the kinetic energy of the mode described by the $(-\hbar^2/2M^*)\nabla^2$ operator, where M^* is some reduced mass, to the potential energy (1). In order to determine the quantitative criterion of the

TABLE V. Frequencies of unstable ferroelectric modes in the high-symmetry phases, energy gains resulting from the lattice distortion,¹ and $\hbar\nu/E_0$ ratios for three ferroelectric phase transitions in SrTiO₃ and CdTiO₃.

Phase transition	ν (cm ⁻¹)	E_0 (meV)	$\hbar\nu/E_0$
SrTiO ₃ , $Pm3m \rightarrow R3m$	68i	0.75	11.2
CdTiO ₃ , $Pbnm \rightarrow Pb2_1m$	81i	1.38	7.28
CdTiO ₃ , $Pbnm \rightarrow Pbn2_1$	104i	6.21	2.08

complete suppression of a phase transition by quantum fluctuations, we consider a simple one-dimensional problem in which a particle of mass M^* moves in a double-well potential $V(x) = -ax^2 + bx^4$. Suppression of the phase transition by quantum fluctuations occurs at the moment when the kinetic energy of zero-point mode vibrations becomes higher than the well depth of the potential barrier under consideration. The numerical solution of the Schrödinger equation shows that this occurs when $b/\sqrt{M^*a^3} > 0.428$. By eliminating the unknown mass M^* from this condition, the criterion can be rewritten in a physically clear form $\hbar\nu/E_0 > 2.419$. Here, $\nu = \sqrt{-2a/M^*}/2\pi$ is the value of an imaginary mode frequency in the high-symmetry configuration (maximum of the potential barrier) determined in the classical (Born–Oppenheimer) approximation, and $E_0 = a^2/4b$ is the depth of the potential well for the $V(x)$ potential. For the four-minimum potential well described by equation (1), the quantitative value of the criterion can be slightly different.

We use the obtained criterion to evaluate the degree of influence of quantum fluctuations on the ferroelectric phase transitions in CdTiO₃. The frequencies of unstable ferroelectric modes determined from first principles in the Born–Oppenheimer approximation, the energies E_0 of the ordered phases, and the $\hbar\nu/E_0$ ratios for the hypothetical ferroelectric phase transition in SrTiO₃ and two phase transitions in CdTiO₃ are given in Table V. It follows from the table that quantum fluctuations should suppress the ferroelectric phase transition in strontium titanate and the transition to the $Pb2_1m$ phase in cadmium titanate. As regards the phase transition to the $Pbn2_1$ phase in cadmium titanate, this transition is susceptible to strong quantum fluctuations but is not completely suppressed. Therefore, the only phase transition that can be associated with the experimentally observed ferroelectric phase transition in CdTiO₃ is that to the $Pbn2_1$ phase.

Quantum fluctuations can also be responsible for the significant discrepancies in the structural positions of atoms and in the values of the spontaneous polarization P_s . In quantum-mechanical calculations of the ground state for multiwell potentials, the displacement corresponding to the most probable atomic position is always smaller than the displacement corresponding to the minimum of the potential energy. Therefore, quantum fluc-

tuations should decrease the distortions accompanying the phase transition and decrease the spontaneous polarization P_s . Other possible factors responsible for the decrease in the experimentally obtained polarization in CdTiO_3 can be the manifestation of twinning in crystals^{8,15,16} and the presence of long-period structures competing with the $Pbnm$ phase.¹⁶

V. CONCLUSIONS

The first-principles calculations of the structural parameters and the phonon spectrum of orthorhombic CdTiO_3 enabled to refine the identification of Raman scattering and IR reflectance spectra. The calculated dependence of the total energy of cadmium titanate on the

amplitudes of two unstable modes indicates that the ferroelectrically distorted $Pbn2_1$ phase is the ground state of the crystal at $T = 0$. This phase appears to be the most stable with respect to quantum fluctuations, which are rather strong and suppress other possible lattice distortions. Quantum fluctuations were found to be one of the main factors responsible for the discrepancy between the calculated and experimentally observed values of spontaneous polarization and structural distortions accompanying the phase transition.

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